

Directly Pd(II)-Bridged Porphyrin Belts with Remarkable Curvatures

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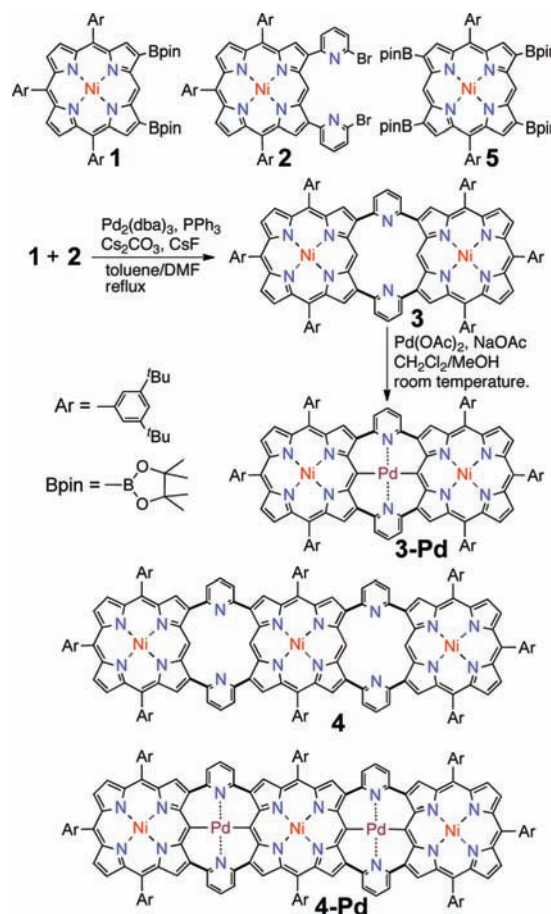
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Abstract: A β,β' -doubly 2,6-pyridylene-bridged porphyrin dimer and trimer were prepared by Suzuki–Miyaura coupling reactions and confirmed to have largely bent structures. These oligoporphyrins were readily metalated via *meso*-C–H bond activation with the assistance of the pyridyl nitrogen atoms to produce the corresponding Pd(II) complexes, which display even larger bent structures and larger TPA values at 800 nm.

Electronically interactive multiporphyrinic systems are promising in light of their π -conjugated properties that are favorable for applications such as optoelectronic devices, sensors, photovoltaic devices, nonlinear optical (NLO) materials, and photodynamic therapy (PDT) pigments.¹ To realize the electronic and photophysical properties required for such applications, exploitation of novel means to manipulate the interporphyrinic interaction is highly desirable. Here we report the synthesis of β,β' -doubly 2,6-pyridylene-bridged Ni(II)-porphyrin arrays that can accommodate Pd(II) metal in the cavity created by two pyridyl moieties.² Interestingly, these porphyrin arrays exhibit remarkably bent conformations due to constraints arising from β,β' -double 2,6-pyridylene bridges. More importantly, the formation of the direct *meso*-to-*meso* metal bridge triggers activation of the electronic interaction between the neighboring porphyrins, hence causing effective delocalization of the π -electronic system.

β,β' -Dipyridyl Ni(II) porphyrin **2** was synthesized by a Suzuki–Miyaura coupling reaction of β,β' -diboryl Ni(II) porphyrin **1**³ and 2,6-dibromopyridine.⁴ Double Suzuki–Miyaura coupling reaction of **2** with **1** afforded **3** in 56% yield (Scheme 1).⁵ Diporphyrin **3** has a preorganized central cavity which would be suitable for metal insertion. In fact, treatment of **3** with Pd(OAc)₂ in the presence of NaOAc in CH₂Cl₂/methanol at room temperature resulted in facile metalation to afford **3-Pd** as an air and moisture stable brown solid in 85% yield. The structures of **3** and **3-Pd** have been assigned by their ¹H NMR and high-resolution electrospray ionization time-of-flight (HR-ESI-TOF) mass spectra.⁵ The final structural confirmation was obtained from single-crystal X-ray diffraction analysis (Figure 1).⁵ Interestingly, the diporphyrin **3** displays a gable structure with a diporphyrin dihedral angle of 106.5°. The pyridyl bridges are held to the neighboring pyrroles with dihedral angles of ca. 47°. In **3-Pd**, Pd(II) insertion decreased the dihedral angle between the pyridyl and porphyrin planes to ca.

Scheme 1. Synthesis of Porphyrin Belts



36° and that between two porphyrins to 87.3°, thus inducing further curving of the dimer. The C–Pd–C and N–Pd–N angles in **3-Pd** were 161° and 157°, respectively.

The UV–vis absorption spectrum of **3** exhibits a slightly broad Soret band at $\lambda_{\max} = 421$ nm (Figure 2) as compared with that of the monomer. In sharp contrast, that of **3-Pd** shows a remarkably perturbed absorption spectrum that spreads over the whole visible region with peaks at 450, 500, 579, and 673 nm. Density functional theory (DFT) calculations revealed distinct differences between the molecular orbitals of **3** and **3-Pd** (Figure S10). One of the degenerated unoccupied MOs (LUMO+1) of **3** is well hybridized with a Pd vacant orbital, forming a highly stabilized LUMO of **3-Pd** delocalized over palladium, *meso*-carbon, and pyridine nitrogen. In contrast, HOMO–2 of **3** which has a_{2u} character with

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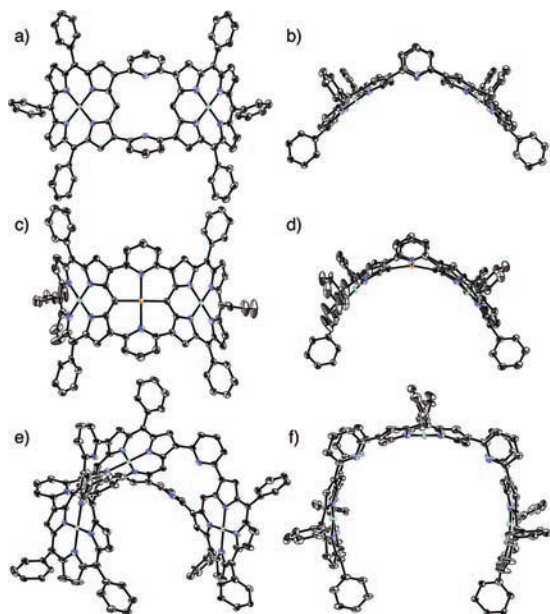


Figure 1. X-ray crystal structures of porphyrin belts. (a) Top view of **3**, (b) side view of **3**, (c) top view of **3-Pd**, (d) side view of **3-Pd**, (e) skew view of **4**, and (f) side view of **4**. The thermal ellipsoids are 50% probability level. *tert*-Butyl groups, solvent molecules, and hydrogen atoms are omitted for clarity.

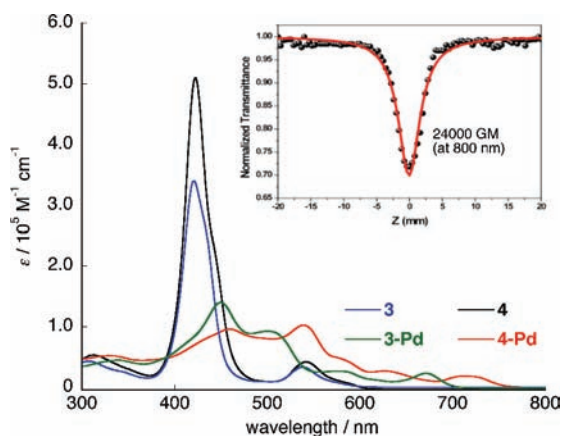


Figure 2. UV-vis absorption spectra of **3**, **3-Pd**, **4**, and **4-Pd** in CH_2Cl_2 . Inset: Open-aperture Z-scan traces of **4-Pd**.

a large MO coefficient on *meso*-carbons is strongly interactive with the filled d_{xz} orbital on Pd, raising the orbital over the original a_{1u} HOMO of **3**. The coplanarization of pyridine and porphyrin also helps this situation, thus resulting in a substantial decrease of the HOMO–LUMO gap by metalation.⁵ These features are supported by electrochemical analysis. The first oxidation potential (vs Ag/Ag⁺) is decreased from 0.75 V for **3** to 0.52 V for **3-Pd**, and the first reduction potential is increased from –1.52 V for **3** to –1.40 V for **3-Pd**, respectively.⁵

In order to expand this synthetic strategy, the cross-coupling reaction of tetraborylporphyrin **5**³ and 2 equiv of **2** was attempted and indeed produced trimer **4** in 13% yield. HR-ESI-TOF mass and ¹H NMR spectra of **4** are fully consistent with the expected structure.⁵ Triporphyrin **4**, judging from the bent structure of **3**, should take a *syn*- or an *anti*-form, which would be difficult to distinguish based on the spectroscopic data. DFT calculations (B3LYP/631SDD) indicate that the *syn*-form is more stable than

the *anti*-form by 3.2 kcal/mol (Figure S11).⁵ The structure of **4** was unambiguously determined by X-ray diffraction analysis to be a remarkably bent *syn*-form that has a large hollow (Figure 1). All the constituent Ni(II) porphyrins take on ruffled conformations with neighboring porphyrins with dihedral angles of 88 and 89°. Metalation of **4** with Pd(OAc)₂ in CH_2Cl_2 furnished **4-Pd** in 75% yield. The absorption spectra of **4** and **4-Pd** are similar to those of **3** and **3-Pd**, suggesting nonconjugative and conjugative features of the arrays, respectively.

The two-photon absorption (TPA) cross section values of the porphyrin belts were measured by using an open-aperture Z-scan method.^{5,6} Laser excitation at 800 nm was chosen to completely eliminate the contribution from one-photon absorption. TPA values were determined for **3** (7000 GM), **3-Pd** (15 700 GM), **4** (17 400 GM), and **4-Pd** (24 000 GM), respectively. In line with the conjugative nature of **3-Pd** and **4-Pd**, their TPA values are larger than those of **3** and **4**, indicating the substantial contribution of the direct C_{meso} –Pd– C_{meso} linkage in the overall π -electronic conjugation.¹

In summary, a β,β' -doubly 2,6-pyridylene-bridged porphyrin dimer and trimer with largely bent structures were constructed by consecutive Suzuki–Miyaura coupling reactions. These oligoporphyrins were readily metalated via double *meso*-C–H bond cleavage with the assistance of the pyridine coordination. The Pd(II)-bridged porphyrin belts display even larger bent structures and larger TPA cross section values at 800 nm. These features are particularly advantageous for future applications in optical devices working in the near-IR region. Recognition of fullerenes by these bent oligoporphyrins⁷ and further extension of this synthetic strategy toward the truly cyclic porphyrin tubes are currently being explored in our laboratories.

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Supporting Information Available: Preparation and analytical data for samples, and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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